**Electronic Supplementary Information**

# An investigation of the role acceptor side chains play in the processibility and efficiency of organic solar cells fabricated from small molecular donors featuring 3,4-ethylenedioxythiophene cores.

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**Supporting Figures**

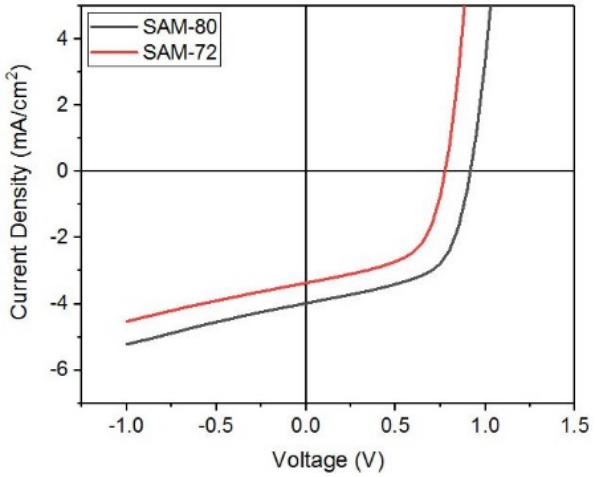



Figure S 1. Current-voltage curves of **SAM-80:$PC_{71}BM$** (1:3 wt%) and **SAM-72:$PC_{71}BM$** (1:5 wt%) devices cast from chloroform.

| | Best PCE (%) | PCE (%) | FF (%) | $J_{sc}$ (mA/cm$^2$) | $V_{oc}$ (V) |
|---|---|---|---|---|---|
| SAM-80:$PC_{71}BM$ (1:3 wt% in chloroform) | **2.10** | **1.78 ± 0.28** | **58.10 ± 0.59** | **3.36 ± 0.54** | **0.91 ± 0.01** |
| SAM-72:$PC_{71}BM$ (1:5 wt% in chloroform) | **1.46** | **1.16 ± 0.21** | **55.90 ± 0.82** | **2.69 ± 0.49** | **0.77 ± 0.00** |

Table S 1. Solar cell performance for the optimum **SAM-80:$PC_{71}BM$** and **SAM-72:$PC_{71}BM$** devices when cast in chloroform.

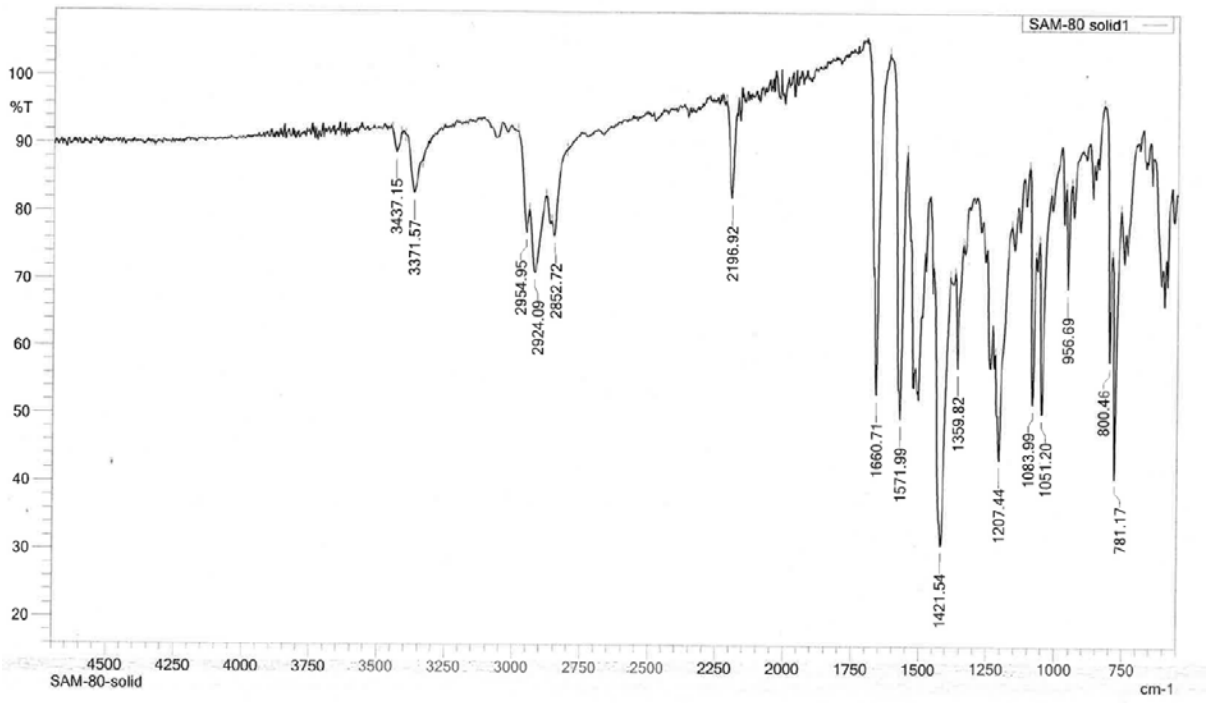



Figure S 2. Solid-state FT-IR spectrum of **SAM-80**. Recorded on IRAffinity-1S Fourier Transform Infrared Spectrophotometer.

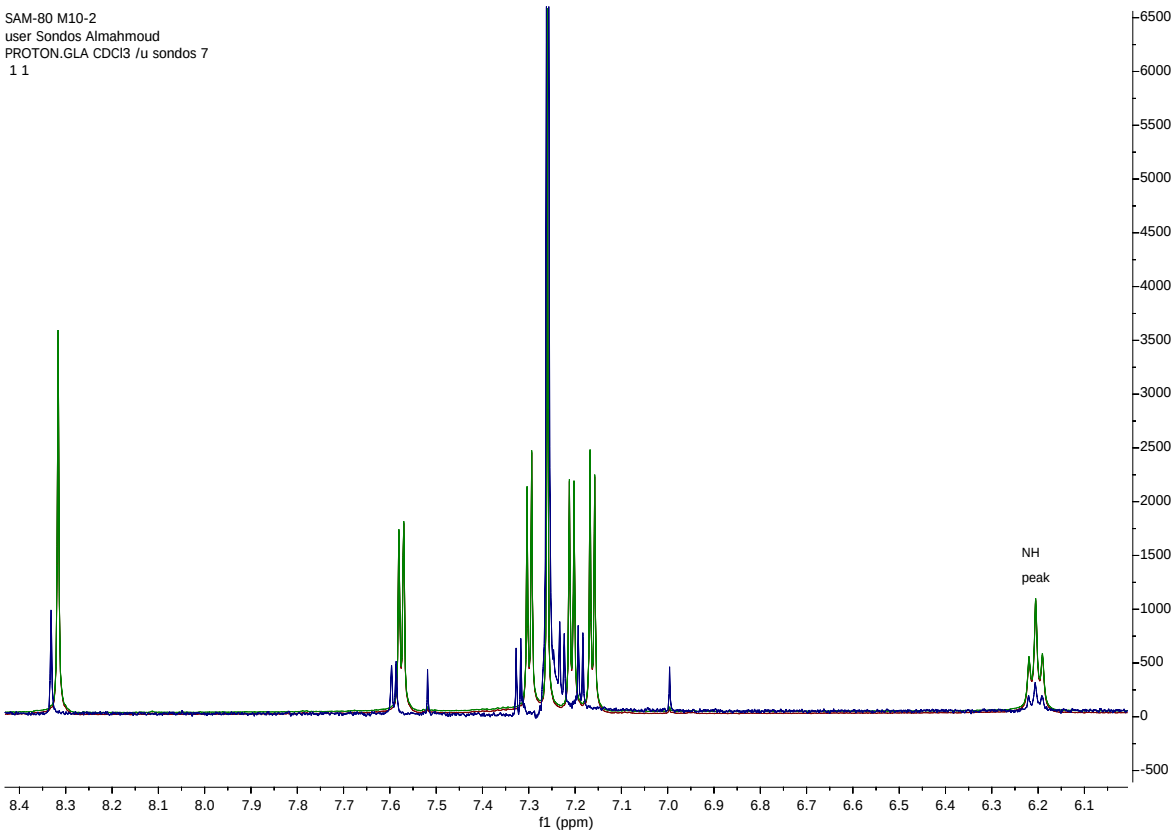
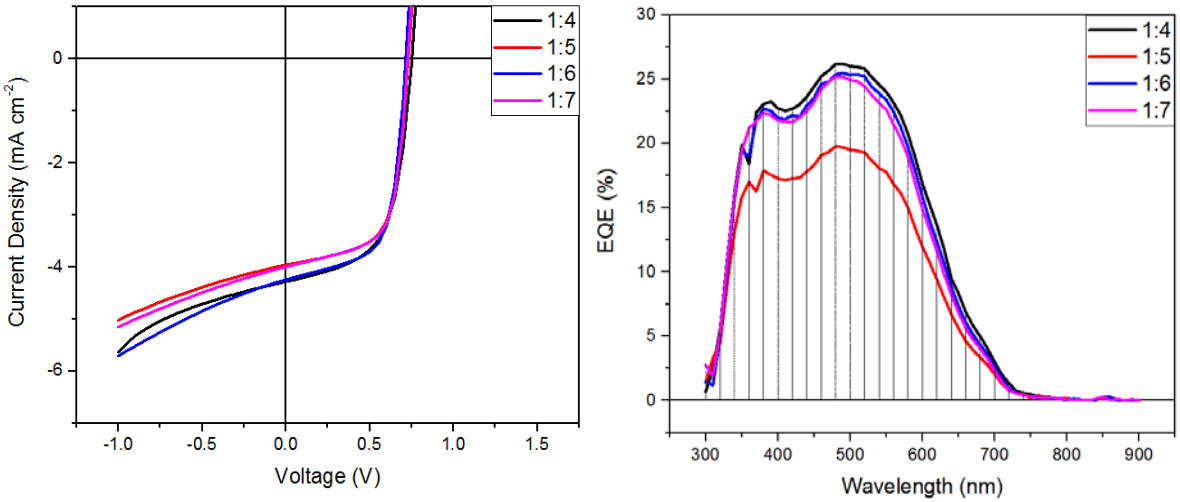



Figure S 3. $^{1}$H NMR of **SAM-80** in $CDCl_3$ using two concentrations $10^{-2}$ M (green) and $10^{-4}$ M (blue).

| D/A weight ratio | Best PCE (%) | PCE (%) | FF (%) | $J_{sc}$ (mA/cm$^2$) | $V_{oc}$ (V) |
|---|---|---|---|---|---|
| 1:4 | **1.92** | **1.69 ± 0.16** | **59.70 ± 0.66** | **3.83 ± 0.34** | **0.74 ± 0.01** |
| 1:5 | **1.88** | **1.73 ± 0.11** | **63.50 ± 1.17** | **3.74 ± 0.17** | **0.73 ± 0.01** |
| 1:6 | **1.96** | **1.73 ± 0.24** | **65.20 ± 0.70** | **3.69 ± 0.45** | **0.72 ± 0.02** |
| 1:7 | **1.90** | **1.58 ± 0.35** | **61.70 ± 3.70** | **3.55 ± 0.53** | **0.72 ± 0.01** |

Table S 2. Solar cell performance for donor to acceptor weight ratio optimization for **SAM-72:PC$_{71}$BM** devices.

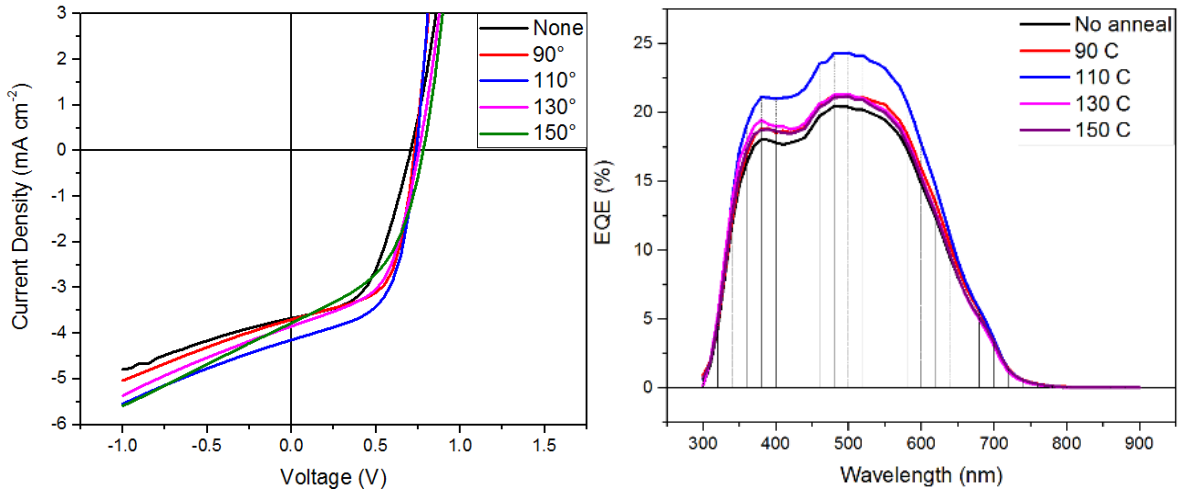



(a) (b)

Figure S 4. (a) Current-voltage plots and (b) EQE spectra for donor to acceptor weight ratio optimization for **SAM-72:PC$_{71}$BM** devices.

| Thermal annealing temp (°C) | Best PCE (%) | PCE (%) | FF (%) | $J_{sc}$ (mA/cm$^2$) | $V_{oc}$ (V) |
|---|---|---|---|---|---|
| No anneal | **1.33** | **1.13 ± 0.12** | **47.35 ± 2.66** | **3.40 ± 0.20** | **0.70 ± 0.01** |
| 90 | **1.62** | **1.32 ± 0.15** | **48.96 ± 6.29** | **3.72 ± 0.20** | **0.73 ± 0.01** |
| 110 | **1.76** | **1.51 ± 0.22** | **52.88 ± 5.27** | **3.86 ± 0.35** | **0.74 ± 0.01** |
| 130 | **1.54** | **1.43 ± 0.13** | **53.18 ± 1.36** | **3.56 ± 0.32** | **0.76 ± 0.00** |
| 150 | **1.37** | **1.29 ± 0.06** | **47.17 ± 1.49** | **3.51 ± 0.26** | **0.78 ± 0.00** |

Table S 3. Solar cell performance for thermal annealing optimization of **SAM-72:PC$_{71}$BM** devices.

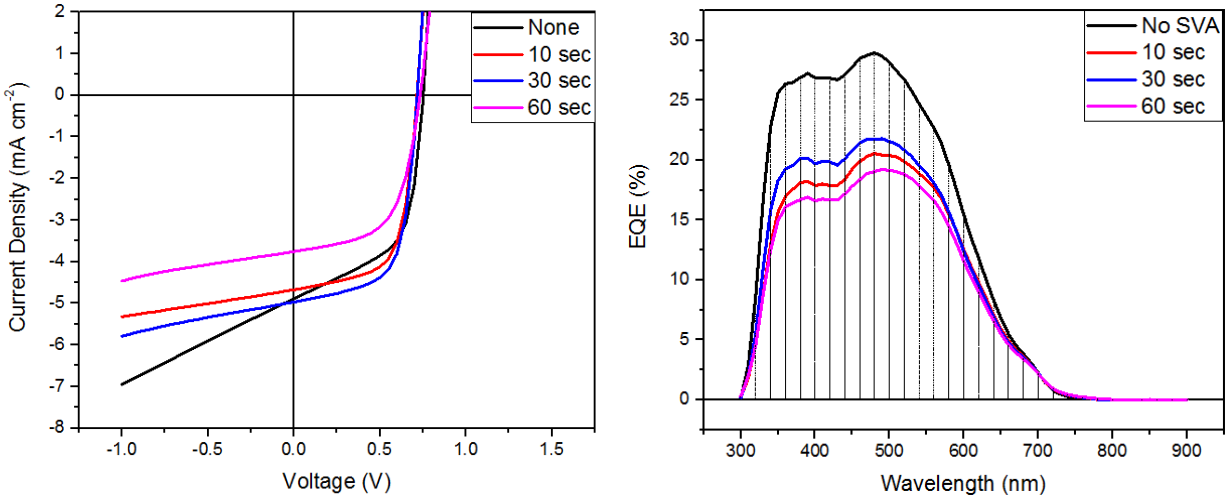



(a) (b)

Figure S 5. (a) Current-voltage plots and (b) EQE spectra for thermal annealing optimization of **SAM-72:PC$_{71}$BM** devices.

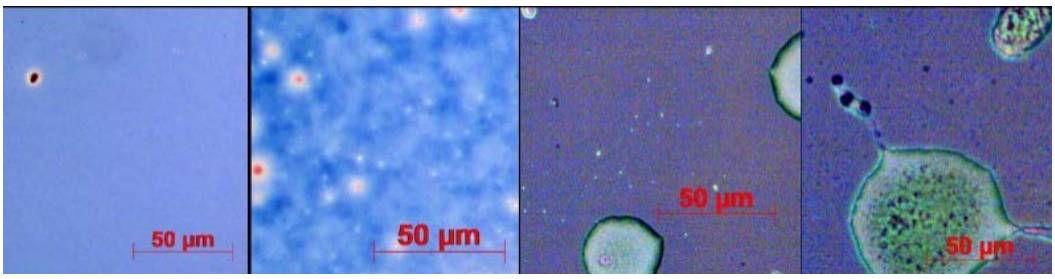
| SVA time (s) | Best PCE (%) | PCE (%) | FF (%) | $J_{sc}$ (mA/cm$^2$) | $V_{oc}$ (V) |
|---|---|---|---|---|---|
| No SVA | **2.10** | **2.00 ± 0.08** | **55.66 ± 2.29** | **4.81 ± 0.28** | **0.75 ± 0.01** |
| 10 | **2.16** | **1.98 ± 0.18** | **65.02 ± 0.93** | **4.27 ± 0.40** | **0.72 ± 0.00** |
| 30 | **2.31** | **2.13 ± 0.15** | **64.24 ± 1.79** | **4.60 ± 0.31** | **0.72 ± 0.00** |
| 60 | **1.62** | **0.97 ± 0.58** | **46.43 ± 12.06** | **2.71 ± 1.18** | **0.73 ± 0.01** |

Table S 4. Solar cell performance for solvent vapor annealing optimization of **SAM-72:PC$_{71}$BM** devices using $CS_2$.



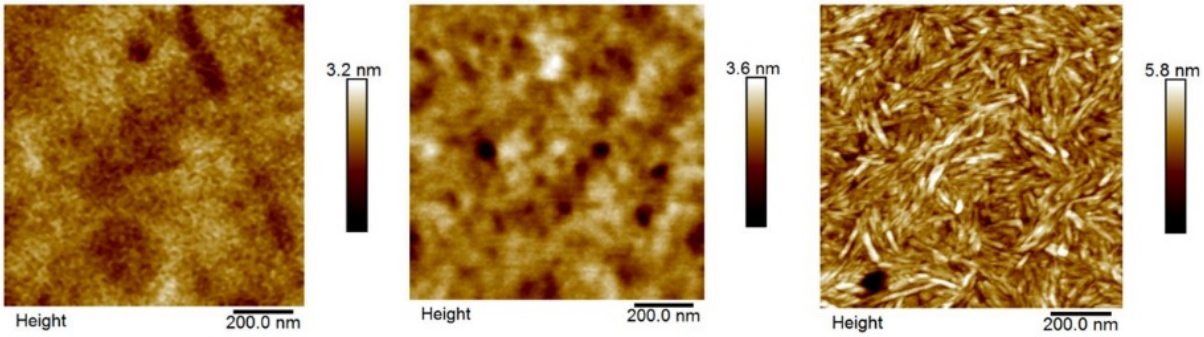

(a) (b)

Figure S 6. (a) Current-voltage plots and (b) EQE spectra for solvent vapor annealing optimization of **SAM-72:PC$_{71}$BM** devices using $CS_2$.




(a) (b) (c) (d)

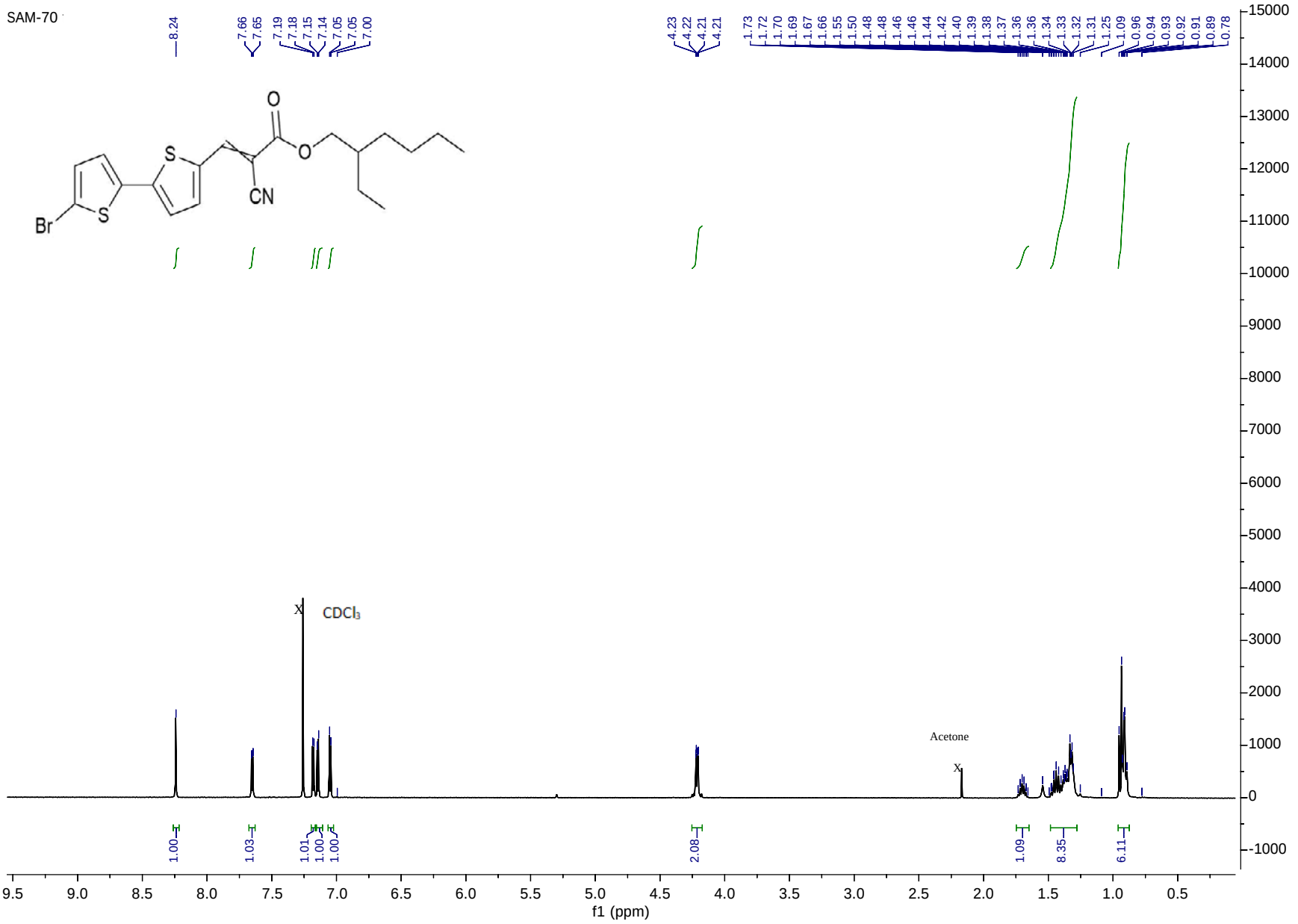
Figure S 7. Optical microscope images of **SAM-72:PC$_{71}$BM** films with 0v% (a), 1v% (b), 3v% (c), and 5v% (d) DIO added to precursor solution.

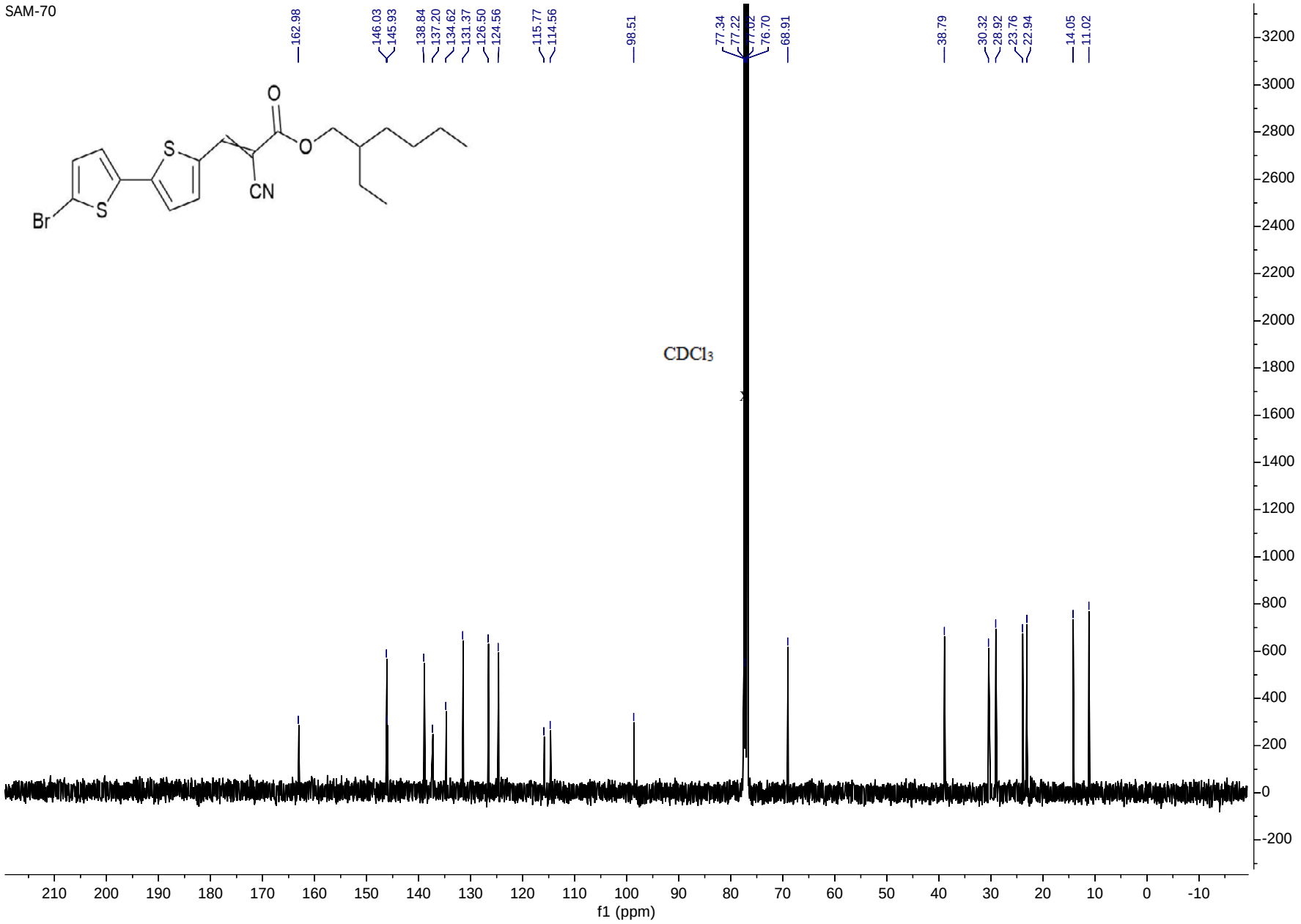


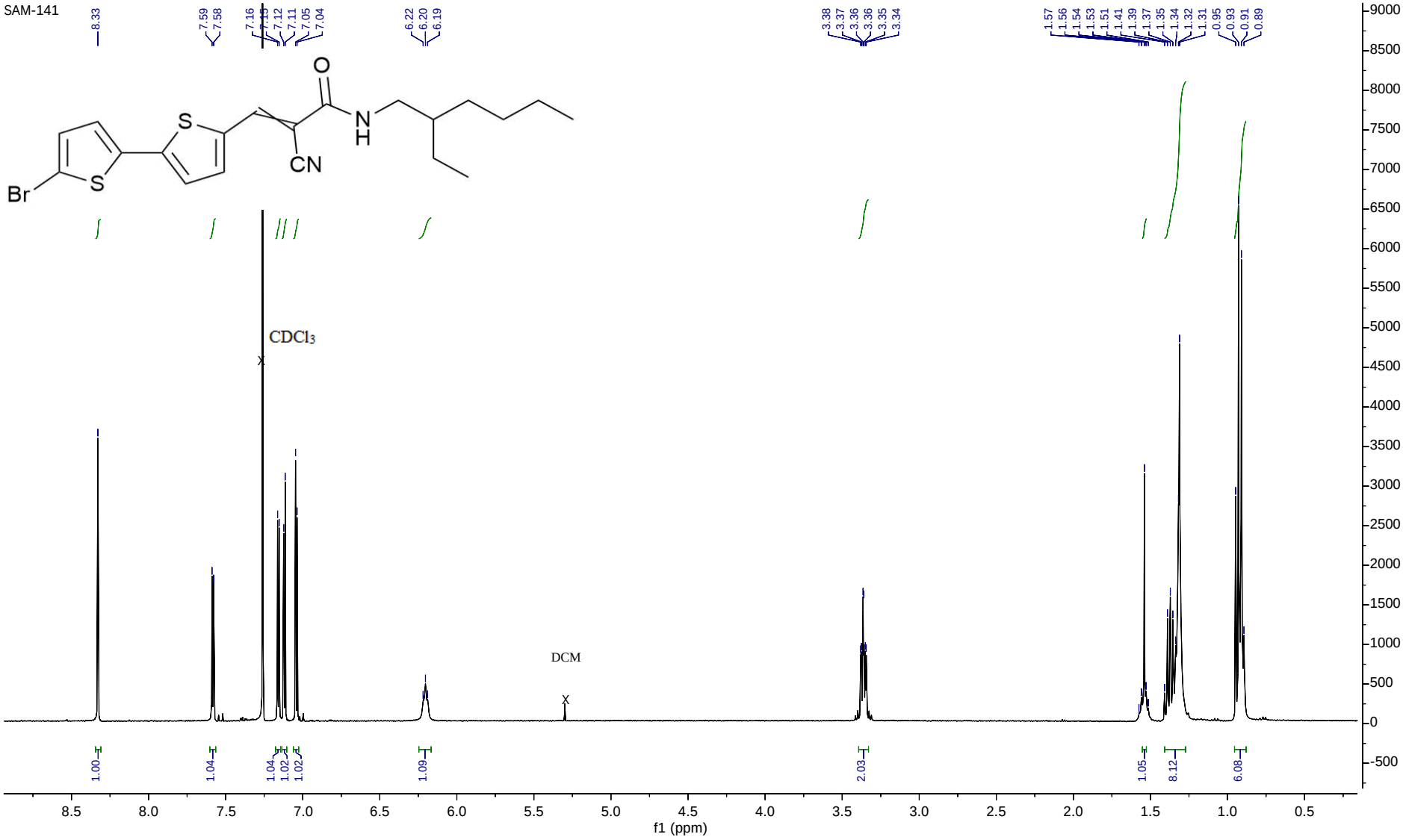

(a) (b) (c)

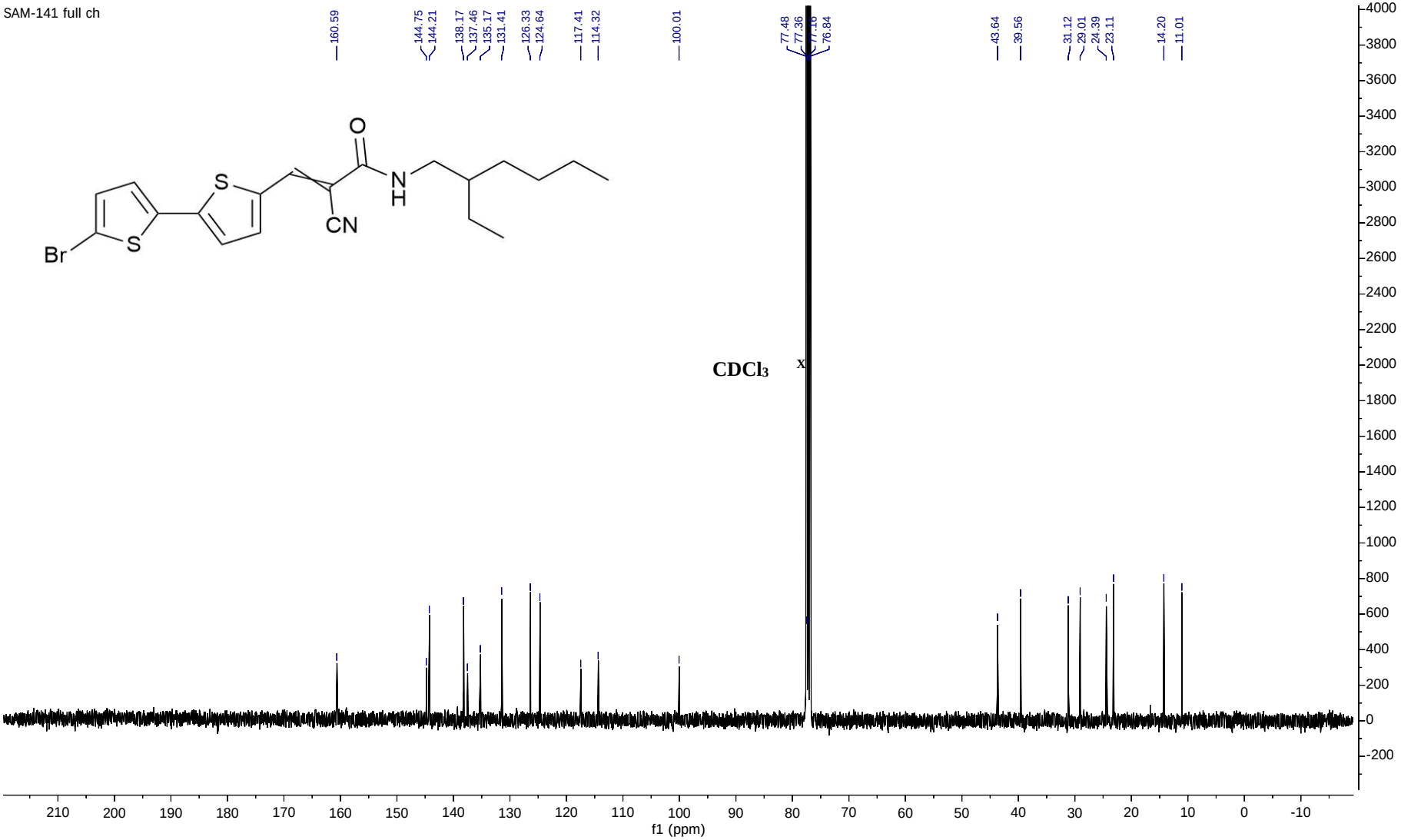
Figure S 8. Height AFM images of **SAM-72:PC$_{71}$BM** films under different processing methods: (a) as cast film with optimized donor and acceptor ratio, (b) thermal annealed film, and (c) film that was both thermally and solvent vapor annealed.

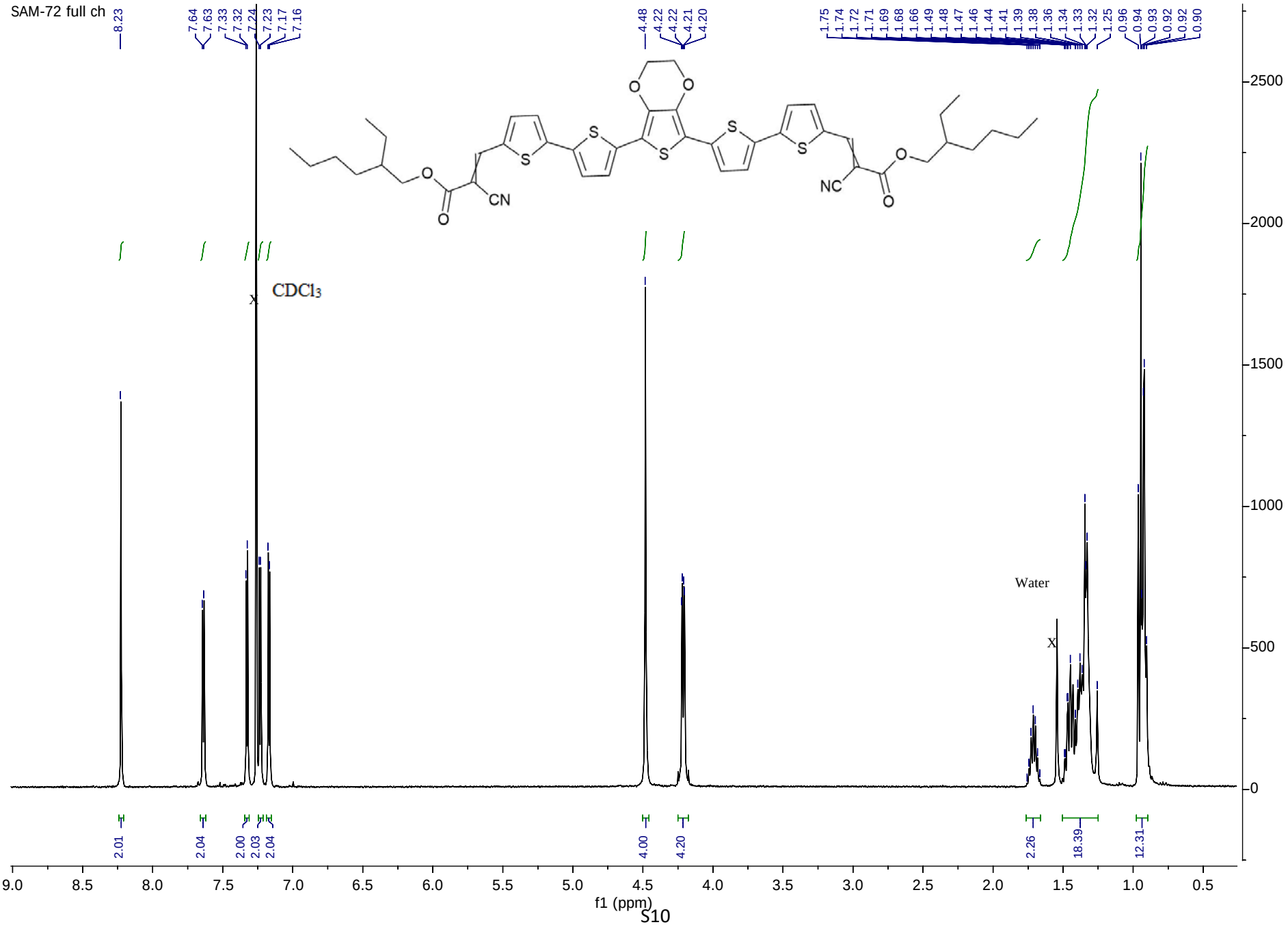
**1H NMR and 13C NMR spectra**

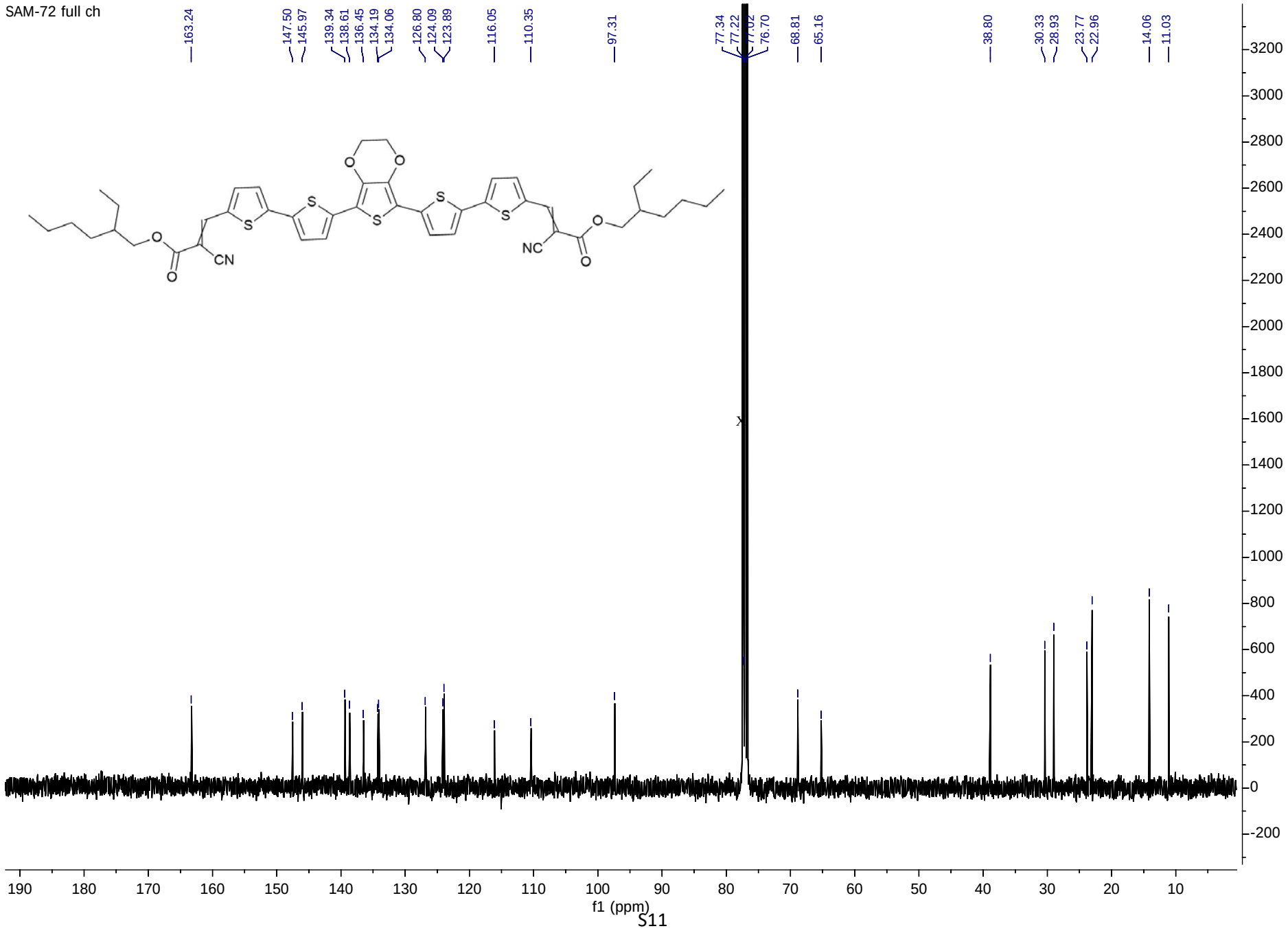


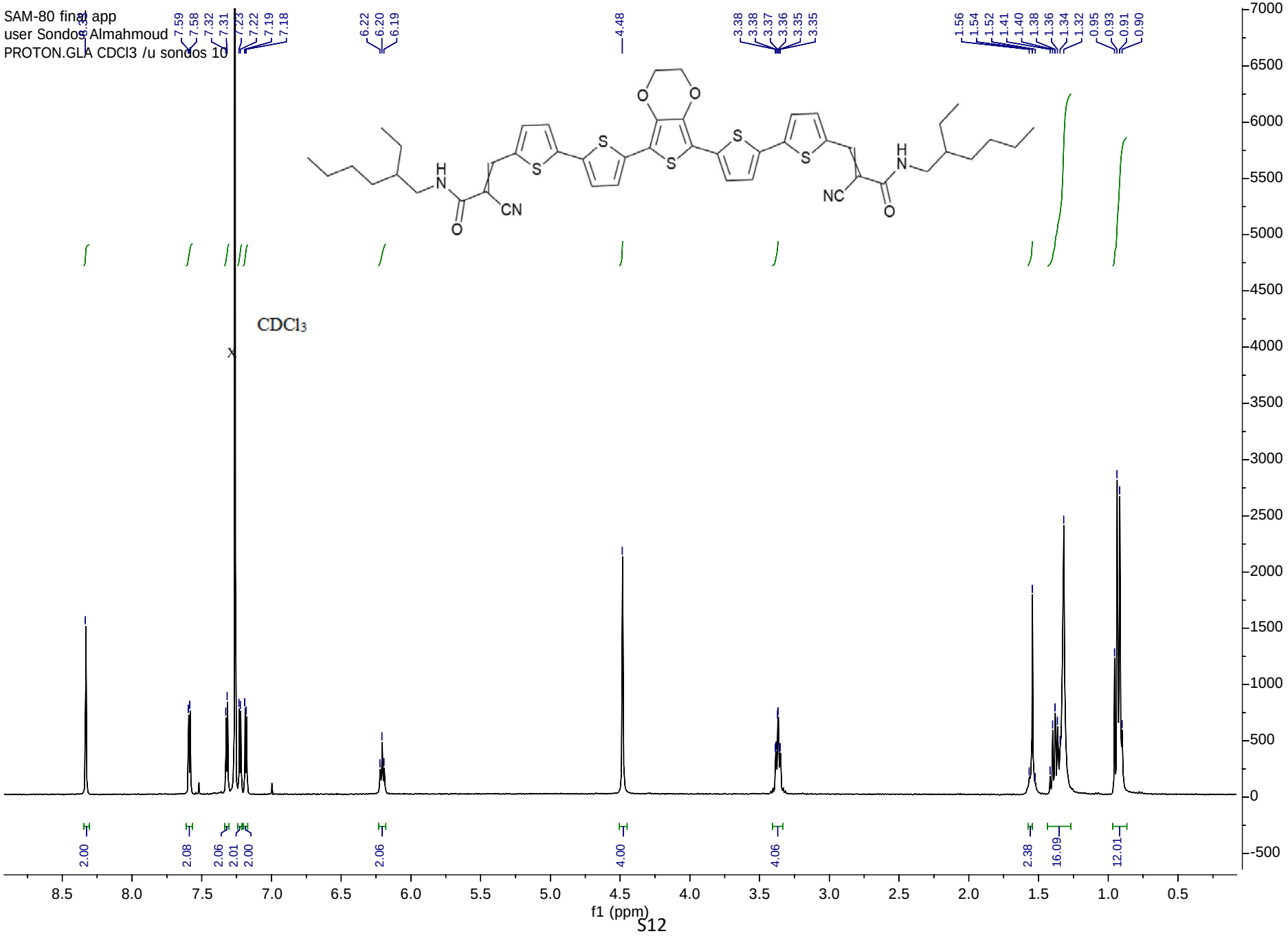

SAM-70
162.98
146.03
145.93
138.84
137.20
134.62
131.37
126.50
124.56
115.77
114.56
98.51
77.34
77.22
77.02
76.70
68.91
38.79
30.32
28.92
23.76
22.94
14.05
11.02
CDCl3
O
S
O
CN
Br
S
f1 (ppm)

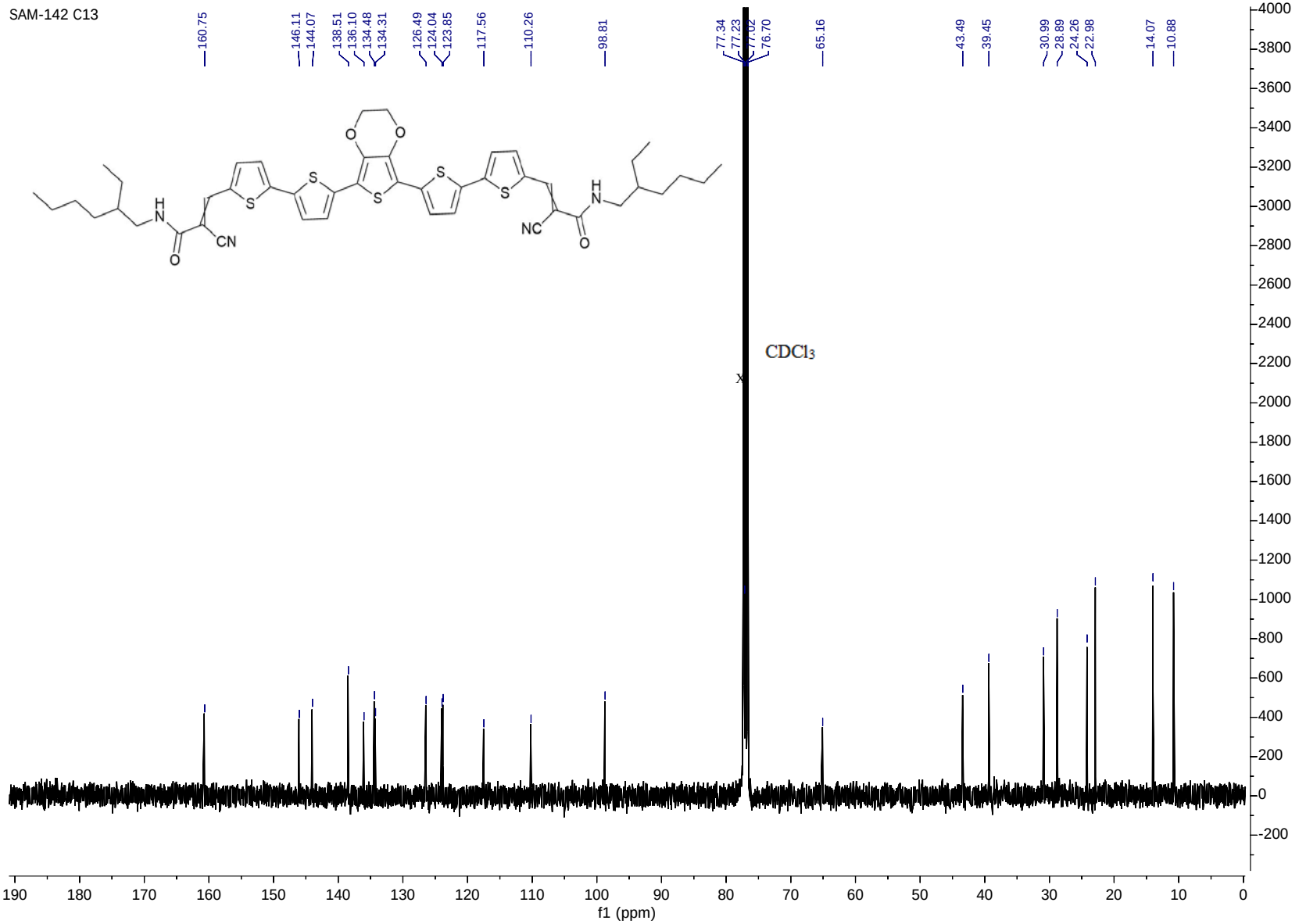

SAM-141
8.33
7.59
7.58
7.16
7.15
7.12
7.11
7.05
7.04
6.22
6.20
6.19
3.38
3.37
3.36
3.36
3.35
3.34
1.57
1.56
1.54
1.53
1.51
1.41
1.39
1.37
1.35
1.34
1.32
1.31
0.95
0.93
0.91
0.89
O
N
H
S
S
Br
CN
CDCl3
DCM
1.00
1.04
1.04
1.02
1.02
1.09
2.03
1.05
8.12
6.08
f1 (ppm)


SAM-141 full ch
160.59
144.75
144.21
138.17
137.46
135.17
131.41
126.33
124.64
117.41
114.32
100.01
77.48
77.36
77.16
76.84
43.64
39.56
31.12
29.01
24.39
23.11
14.20
11.01
O
S
N
H
CN
S
Br
CDCl3
f1 (ppm)


SAM-72 full ch
8.23
7.64
7.63
7.33
7.32
7.24
7.23
7.17
7.16
4.48
4.22
4.22
4.21
4.20
1.75
1.74
1.72
1.71
1.69
1.68
1.66
1.49
1.48
1.47
1.46
1.44
1.41
1.39
1.38
1.36
1.34
1.33
1.32
1.25
0.96
0.94
0.93
0.92
0.92
0.90
O
O
O
O
S
S
S
S
CN
NC
O
O
CDCl3
Water
2500
2000
1500
1000
500
0
2.01
2.04
2.00
2.03
2.04
4.00
4.20
2.26
18.39
12.31
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


SAM-72 full ch
163.24
147.50
145.97
139.34
138.61
136.45
134.19
134.06
126.80
124.09
123.89
116.05
110.35
97.31
77.34
77.22
77.02
76.70
68.81
65.16
38.80
30.33
28.93
23.77
22.96
14.06
11.03
CN
NC
f1 (ppm)


SAM-80 final app
user Sondos Almahmoud
PROTON.GLA CDCl3 /u sondos 10
CDCl3
f1 (ppm)


SAM-142 C13
160.75
146.11
144.07
138.51
136.10
134.48
134.31
126.49
124.04
123.85
117.56
110.26
98.81
77.34
77.23
77.02
76.70
65.16
43.49
39.45
30.99
28.89
24.26
22.98
14.07
10.88
CDCl3
f1 (ppm)